JC10 Rec'd PCT/PTO 25 JAN

Form PTO-1390 P21955.P01	U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER P21955
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		U.S. APPLICATION NO (If known, see 37 CFR 1.5) 10/031933
INTERNATIONAL APPLICATION NO. PCT/EP00/06766	INTERNATIONAL FILING DATE 15 July 2000	PRIORITY DATE CLAIMED 27 July 1999

TITLE OF INVENTION

LITHIUM INTERCALATION COMPOUNDS CONTAINING LITHIUM MANGANESE OXIDE

APPLICANT(S) FOR DO/EO/US

Claudius KORMANN

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. _X_ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ___ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. _X_ This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)).
4. _X_ The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
5. _X_ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. _X_ is attached hereto (required only if not communicated by the International Bureau)
   b. ___ has been communicated by the International Bureau.
   c. ___ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. _X_ An English language translation of the International Application as filed (35 U.S.C. 371 (c)(2)).
7. ___ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ___ are attached hereto (required only if not communicated by the International Bureau).
   b. ___ have been communicated by the International Bureau.
   c. ___ have not been made, however, the time limit for making such amendments has NOT expired.
   d. ___ have not been made and will not be made.
8. ___ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3))
9. _X_ An oath or declaration of the inventor(s) (35 U.S.C. .371(c)(4)).
   "Unexecuted"
10. ___ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (U.S.C. 371(c)(5)).

Items 11 to 16 below concern other document(s) or information included:

11. Assignee: ~~AMTEC MAGNETICS GMBH of Ludwigshafen, GERMANY~~
12. ___ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
13. ___ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
14. _X_ A FIRST preliminary amendment.
    ___ A SECOND or SUBSEQUENT preliminary amendment.
15. ___ A substitute specification.
16. ___ A change of power of attorney and/or address letter.
17. _X_ Figure of Drawing to be published ___1___
18. _X_ Other items or information:
    Cover Sheet and International Application as published(in German).
    PCT/IPEA/416(in German).
    PCT/IPEA/409(in German).
    PCT/ISA/210(in German and English).
    Cover Letter under 35 U.S.C 371 and 1.495.
    Claim of Priority.

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U.S. APPLICATION NO (If known, see 37 CFR 1.5) 10/031933	INTERNATIONAL APPLICATION NO PCT/EP00/06766	ATTORNEY'S DOCKET NUMBER P21955

				CALCULATIONS	PTO USE ONLY
19. _X_ The following fees are submitted Basic National Fee (37 CFR 1 492(a)(1)-(5)): Search report has been prepared by the EPO or JPO. . . . . $ 890.00 International preliminary examination fee paid to USPTO (37 CFR 1.482). . . . . $ 710.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO(37 CFR 1.445(a)(2). . . . . $ 740.00 Neither international preliminary examination fee (37 CFR 1 482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO. . . . .$1,040 00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4). . . . .$ 100.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				$890.00	
Surcharge of $130 00 for furnishing the oath or declaration later than ___ 20 ___ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				$	
Claims	Number Filed	Number Extra	RATE		
Total Claims	20 - 20 =	0	X $18 00	$0.00	
Independent Claims	1 - 3 =	0	X $84.00	$0 00	
Multiple dependent claim(s) (if applicable)			+ $280.00	$	
TOTAL OF ABOVE CALCULATIONS =				$$890.00	
___ Applicant claims small entity status. See 37 CFR 1 27. The fees indicated above are reduced by ½.				$	
SUBTOTAL =				$890.00	
Processing fee of $130.00 for furnishing the English translation later than ___ 20 ___ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +					
Extension of Time fee in the amount of $					
TOTAL NATIONAL FEE =				$890.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h) The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40.00 per property +					
TOTAL FEES ENCLOSED =				$890.00	
				Amount to be refunded	$
				Charged	$

a. _X_ A check in the amount of $890.00 to cover the above fees is enclosed.

b. ___ Please charge my Deposit Account No. _____ in the amount of $_____ to cover the above fees.

c. _X_ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 19-0089.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO **CUSTOMER NO. 7055**
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SIGNATURE
Neil F. Greenblum
NAME
28,394 Reg. no. 33,094
REGISTRATION NUMBER

P21955.A02

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Claudius KORMANN

Group Art Unit: Unknown

Appl. No. : Not Yet Assigned (National Stage of PCT/EP00/06766)

Examiner: Unknown

I.A. Filed : July 15, 2000

For : LITHIUM INTERCALATION COMPOUNDS CONTAINING LITHIUM MANGANESE OXIDE

PRELIMINARY AMENDMENT

Assistant Commissioner of Patents
Washington, D.C. 20231

Sir:

Prior to calculation of the filing fees and examination of the above-identified patent application, entry of the following amendment is respectfully requested.

IN THE CLAIMS

Please amend claims 3-7, 11, 14 and 16, as follows (a marked-up copy of the changes is attached in an Appendix to the present amendment):

3. (Amended) A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 1 and 2] claim 1, where the specific BET surface area is from 0.5 to 1.9 m^2/g.

4. (Amended) A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 1 and 2] claim 1, where the specific BET surface area is from 0.6 to 1.5 m^2/g.

5. (Amended) A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 1 to 4] claim 1, where the particle size, determined from the d_{50} value, is greater than 1 μm.

6. (Amended) A lithium intercalation compound having a spinel structure and containing lithium manganese oxide as claimed in [claims 1 to 5] claim 1, where the diameter, determined from the d_{90} value, is less than 25 μm.

7. (Amended) A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 1 to 5] claim 1, where the diameter, determined from the d_{90} value, is less than 20 μm.

11. (Amended) A process for the preparation of a lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 8 to 10] claim 8, where the particulate, crystalline spinel precursor compound consists of the three phases MnO, $LiMnO_2$ and Mn_3O_4.

14. (Amended) A process as claimed in [one of claims 8 to 13] claim 8, where, after the heating in an oxidizing atmosphere, the resultant solid is suspended in water with addition of one or more alkaline lithium compounds, and the suspension is spray-dried at a temperature of from 100°C to 400°C.

16. (Amended) A process as claimed in [one of claims 8 to 15] claim 8, where the intimate mixing is carried out in the presence of a sintering aid in a concentration of from 0.1 to 3%, based on the weight of the solids employed.

P21955.A02

REMARKS

The Examiner is respectfully requested to enter the foregoing amendment to remove multiple dependent claims prior to examination of the above-identified patent application.

The amendments to the claims made in this amendment have not been made to overcome the prior art, and thus, should be considered to have been made for a purpose unrelated to patentability, and no estoppel should be deemed to attach thereto.

Should there be any questions, the Examiner is invited to contact the undersigned at the below-listed telephone number.

Respectfully submitted,
Claudius KORMANN

Neil F. Greenblum
Reg. No. 28,394 Reg. No. 33,094

January 25, 2002
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P21955.A02

APPENDIX
MARKED-UP COPY OF CHANGES TO CLAIMS

3. (Amended) A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 1 and 2] <u>claim 1</u>, where the specific BET surface area is from 0.5 to 1.9 m^2/g.

4. (Amended) A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 1 and 2] <u>claim 1</u>, where the specific BET surface area is from 0.6 to 1.5 m^2/g.

5. (Amended) A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 1 to 4] <u>claim 1</u>, where the particle size, determined from the d_{50} value, is greater than 1 μm.

6. (Amended) A lithium intercalation compound having a spinel structure and containing lithium manganese oxide as claimed in [claims 1 to 5] <u>claim 1</u>, where the diameter, determined from the d_{90} value, is less than 25 μm.

7. (Amended) A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in [claims 1 to 5] <u>claim 1</u>, where the diameter, determined from the d_{90} value, is less than 20 μm.

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14. (Amended) A process as claimed in [one of claims 8 to 13] claim 8, where, after the heating in an oxidizing atmosphere, the resultant solid is suspended in water with addition of one or more alkaline lithium compounds, and the suspension is spray-dried at a temperature of from 100°C to 400°C.

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Lithium intercalation compounds containing lithium manganese oxide

Description

The invention relates to improved lithium intercalation compounds containing lithium manganese oxide and having a spinel structure for thin-film electrodes, to a process for their preparation, to electrodes produced therefrom, and to secondary lithium ion batteries containing lithium intercalation compounds containing lithium manganese oxide as active material of the positive electrode.

Lithium ion batteries can be made from one or more electrochemical cells which contain electrochemically active pigments. Cells of this type typically consist of an anode (negative electrode), a separator, a cathode (positive electrode) and an electrolyte. Batteries containing metallic lithium as anode are known, as are those containing graphite, coke or other carbon particles which, as is known, are able to intercalate alkali metal ions. Also known are batteries containing other lithium intercalation compounds, i.e. substances which are able to incorporate and release lithium under the action of an electric potential. The electrolyte typically consists of a lithium salt dissolved in one or more aprotic, normally organic solvents. Further suitable electrolytes are solid electrolytes which consist of a polymeric matrix containing an ionically conductive, but electronically insulating medium. The charging process is generally defined in such a way that the anode (the negative pole) takes up lithium ions during charging, while the cathode (the positive pole) serves as a source of lithium ions. Cells containing lithium metal as anode are usually charged during assembly.

Cells with anodes containing graphite or other carbon or another host substance which is capable of taking up lithium ions are usually uncharged during assembly. In order that they can be used as energy stores, they must be connected and charged against an intercalation compound containing lithium ions, preferably an intercalation compound containing lithium oxide. During charging, the lithium ions migrate from the intercalation compound to the graphite or carbon or another host substance which is capable of taking up lithium ions. The cell can then be discharged again, during which the lithium moves back. Rechargeable batteries of this type which do not contain metallic lithium are known as lithium ion batteries. Examples thereof are described in US 4,464,447 and US 5,418,090.

$LiCoO_2$, $LiMn_2O_4$ and $LiNiO_2$ are preferably employed as oxidic materials in the cathodes. All these compounds are also employed with varied mixing ratios of the metal ions in order to establish certain advantages in charging or in the service life. Some or all of the oxygen is sometimes replaced by other elements, for example fluorine or sulfur. While the cobalt compounds are expensive, the nickel compounds are difficult to prepare. By contrast, manganese compounds are relatively cheap.

The specific charge of $LiMn_2O_4$ is theoretically 148 milliampere hours per gram. This value can be changed by varying the oxygen content or the ratio between the lithium and the manganese. In the opinion of many experts, however, $LiMn_2O_4$ can only reversibly cycle about 110-120 milliampere hours per gram, corresponding to about 0.8 mol of lithium per formula unit, in the long term. In the case of $LiNiO_2$ and $LiCoO_2$, only about 0.5 mol of lithium per formula unit can be reversibly

cycled. The situation is more favorable in the case of mixed nickel oxides, in which some of the nickel has been replaced by cobalt or another metal, metalloid or transition metal. Mention may be made by way of example of $Li_1Ni_{0.85}Co_{0.15}O_2$. The use of integer coefficients 1 for lithium or 2 for oxygen serves only to simplify the formula description; in practice, fractional values are also used due to intentional or unintentional variation of the amounts of starting materials. Experience teaches that the elements can be varied in broad – not only even numbered – mixing ratios, giving intercalation compounds which are suitable for use in cathodes. It is essential that the compounds contain lithium ions and elements that are sufficiently capable of changing their electric charge.

In the meantime, many processes for the preparation of intercalation compounds for use in cathodes have been described. Thus, US 4,302,518 describes the synthesis of $Li_xCo_yO_2$ by heating a mixture of lithium carbonate and cobalt carbonate at 900°C in air, followed by two further heating steps. US 4,507,371 teaches that lithium intercalation compounds having the cubic ion lattice $(B_2)X_4^{n-}$ can be synthesized by various reactions: solid-state reactions from the pulverulent elements or compounds thereof at high temperatures, ion exchange methods or chemical or electrochemical titration techniques. US 4,980,080 describes a process for the preparation of $LiNi_{1-x}Co_xO_2$ which comprises the following steps:

1) preparation of a mixture of powders,

2) heating the mixture in air at 600-800°C

3) optionally: homogenization of the heated product and repetition of the powder heating.

A wet-chemical process for the preparation of a lithium manganese oxide spinel is described in DE 19 515 629. Here, a lithium compound and a manganese salt are reacted in the disperse phase and dried, after which the dry residue is subjected to a sequence of grinding and heating steps. A further wet-chemical synthetic process is described in US 5,742,070. It is essentially based on the preparation of solutions of lithium, transition metal and organic acids and alcohols, which are subsequently dried, ground and heated.

PCT Application WO 97/37935 claims a dry preparation process in which mixtures of manganese oxides and lithium compounds, each with a controlled particle size distribution, are repeatedly heated at selected temperatures. PCT application WO 98/02931 describes a process for the preparation of lithium manganese intercalation oxides which consists of the reaction of LiOH, MnO_2 and at least one polyfunctional alcohol followed by heat treatment. However, the known preparation processes for lithium manganese oxide pigments require either expensive raw materials, such as readily soluble manganese compounds, or complex process steps in order to meet the high demands made of lithium manganese oxide pigments for use in electrodes. In particular, no suitable process was known for the preparation of smooth lithium manganese oxide pigments which are suitable for use in particularly thin-layered electrodes.

The present invention therefore had the object of providing lithium manganese oxide intercalation compounds having a spinel structure and having a high specific charge density which are suitable for use in particularly thin-layered electrodes for high-performance secondary lithium ion batteries. A further

object consisted in providing a simple process for the preparation of lithium manganese oxide intercalation compounds of this type. A further object consisted in the provision of thin film electrodes which are suitable for use in high-performance secondary lithium ion batteries. An additional object consisted in providing secondary lithium ion batteries which have high performance and are inexpensive, environmentally friendly and safe.

The object according to the invention has been achieved by the provision of lithium intercalation compounds containing lithium manganese oxide and having a spinel structure for thin-film electrodes, where the lithium intercalation compounds have a particularly smooth and highly crystalline morphology, a specific surface area, determined by the BET method, of from 0.3 to 5 m^2/g, a particle size, determined from the d_{50} value, of greater than 0.5 μm, a diameter, determined from the d_{90} value, of 30 μm or less, and an internal pore volume of < 0.05 ml/g and have a pronounced crystal structure.

The term "morphology" here is taken to mean the interaction of the particle properties porosity (pore size and volume), particle size (diameter) and specific surface area.

It has furthermore been found that lithium manganese oxide intercalation compounds of this type can be prepared using a process which comprises:

a) preparation of an intimate mixture of one or more lithium compounds and one or more manganese compounds, where at least one of these compounds or the sum of all compounds contains sufficient active oxygen that the number of equivalents of active oxygen is equal to or greater than the

number of lithium atoms, and heating at from 600°C to 1000°C in a non-oxidizing atmosphere, followed by grinding, giving a particulate, crystalline spinel precursor compound;

b) heating the crystalline spinel precursor compound in an oxidizing atmosphere at from 500°C to 800°C with a residence time of from 0.5 to 10 hours.

It has also been found that thin-film electrodes which contain lithium manganese oxide intercalation compounds having a spinel structure prepared by the process according to the invention achieve a high specific charge density and high performance in secondary lithium ion batteries. Thin-film electrodes of this type are produced by general processes which are known per se, for example by spraying, knife coating and pressing of mixtures of the lithium manganese oxide intercalation compound according to the invention, conductive pigment and binder, if desired as a mixture with suitable solvents and further additives, onto a metallic, electrically conducting, thin foil or another suitable collector.

It has furthermore been found that secondary lithium ion batteries which contain the lithium manganese oxide intercalation compounds according to the invention as active material of the positive electrode have high performance and at the same time are inexpensive to produce, are safe and are environmentally friendly.

Secondary lithium ion batteries of this type are produced in a manner known per se and essentially consist of a positive electrode, a negative electrode, a separator and an electrolyte in a casing. For the secondary lithium ion batteries according to the invention, the lithium manganese oxide intercalation

compounds according to the invention are used as active material with a suitable binder known per se in the positive electrode, while the active material employed for the negative electrode is graphite or carbon or another host substance which is capable of taking up lithium ions, with a suitable binder known per se.

The lithium manganese oxide intercalation compounds having a spinel structure according to the invention are distinguished by particularly good processing and electrical properties. They are suitable for use in particularly thin-layered electrodes. The specific surface area of the lithium manganese oxide intercalation compounds according to the invention is in the range 0.3 - 5 m^2/g, preferably 0.5 - 1.9 m^2/g and very preferably 0.6 - 1.5 m^2/g. The particle size, measured from the d_{50} value, is greater than 0.5 μm, preferably greater than 1 μm. The diameter of the particles is advantageously not greater than d_{90} = 30 μm, preferably less than d_{90} = 25 μm, very preferably less than d_{90} = 20 μm. The particles are essentially free from internal pores. Internal pores are defined as follows: the size of the internal pores $d_{internal}$ depends on the particle size d_{50}. Internal pores are always the same size as or smaller than a quarter of the particle size d_{50} and are of equal size or larger than 0.01 μm. The following correlation thus arises for the size range of the internal pores:

$$0.01\ \mu m \leq d_{internal} \leq d_{50}/4.$$

The internal pore volume is the cumulative pore volume of pores in this size range. The lithium manganese oxide particles according to the invention are particularly smooth and have a low internal pore volume of less than 0.05 ml/g and preferably less than 0.03 ml/g.

In addition, the lithium manganese oxide intercalation compounds according to the invention are very crystalline, which is evident from very sharp diffraction reflections in the diffractograms. Sharp diffraction reflections are generally formed in the case of large crystallite sizes.

The process according to the invention for the preparation of lithium manganese oxide intercalation compounds having a spinel structure consists at least of two steps:

I. the preparation of a particulate, crystalline precursor compound by intimate mixing of the starting materials, heating in a non-oxidizing atmosphere and subsequent grinding;

II. heating in an oxidizing atmosphere, in which the particulate, crystalline spinel precursor compound is converted into the smooth, highly crystalline lithium manganese oxide intercalation compound having a spinel structure according to the invention.

The synthesis of a lithium manganese oxide having the morphology according to the invention by the process according to the invention is described below:

1.1. Mixing of the starting materials Li_2CO_3 and manganese oxide Mn_3O_4. Suitable starting materials for the preparation of the lithium manganese oxide according to the invention are also various other known manganese and lithium compounds, for example Li_2O_2, Mn_2O_3 or MnO_2, or mixtures of lithium oxides or manganese oxides, so long as the mixture contains sufficient active oxygen. The preferred

manganese compound is Mn_3O_4 and the preferred lithium compound is Li_2CO_3. The active oxygen promotes the linking of lithium to manganese during firing. The amount (number of equivalents) of active oxygen must be at least as large as the number of lithium atoms. Active oxygen can be introduced by the manganese compound so long as the manganese valency is greater than 2. Each Mn valency greater than 2 supplies one equivalent of active oxygen, each Mn valency greater than 3 supplies two equivalents of active oxygen, etc. Active oxygen can also be introduced by the lithium compound, where each formal Li valency greater than 1 (for example Li_2O_2) supplies one equivalent of active oxygen. The mixing process generally takes between 10 and 60 minutes, but preferably from 15 to 45 minutes. Mixers which can be employed here are all customary types of mixer, preferably mixers with integrated grinding tools.

1.2. Heating of the mixture in a non-oxidizing atmosphere, advantageously in a rotary tube furnace, preferably under N_2, argon or another essentially oxygen-free gas at 600°C - 1000°C with a residence time of from 15 to 120 minutes. The heating is preferably carried out under nitrogen at a temperature of from 700°C to 900°C and a residence time of from 30 to 90 minutes. During this heating, the process conditions are set in such a way that exclusively the three phases MnO, $LiMnO_2$ and Mn_3O_4 are formed. A non-oxidizing atmosphere can also be obtained by establishing oxygen-eliminating reaction conditions, i.e. reaction conditions under which the oxygen content of the mixture employed drops.

1.3. Grinding of the heated mixture until a finely divided mixture is obtained. Suitable mills here are, for example, tin mills, impact disk mills, universal mills, jet mills or the like, optionally with classification. It is also possible to carry out a plurality of grinding processes one after the other in identical or different mills.

1.4. Optional additional step: reheating as in point 1.2, where the temperature may be the same as or higher than in point 1.2, but is not higher than 1000°C and is preferably not higher than 950°C. The residence time is likewise from 15 to 120 minutes.

1.5. Optional additional step: regrinding as in point 1.3, where the same or a different mill as in 1.3 can be selected and particle sizes and particle size distributions the same as or different from 1.3 are achieved.

2. Heating of the particulate, crystalline spinel precursor compound under an oxidizing atmosphere at 500°C - 800°C with a residence time of from 0.5 to 10 hours. The heating here can be carried out in a rotary tube furnace, preferably at from 700°C to 800°C and - if the furnace is fitted with a plurality of heating zones - at a reduced temperature of 450°C - 750°C in the final heating zone. The residence time in the heating zone is preferably 0.5 - 6 hours. The oxidizing atmosphere is preferably produced with oxygen. The heating can likewise be carried out in a stationary furnace under an oxidizing atmosphere at a preferred temperature of from 650°C to 750°C with a residence time of preferably greater than 5

hours. Here too, the oxidizing atmosphere is preferably produced with oxygen.

3. Optional addition step: suspension of the lithium manganese oxide intercalation compound having a spinel structure in water with addition of one or more alkaline lithium salts, followed by spray-drying at temperatures of from 100°C to 400°C. Suitable alkaline aluminum salts are, for example, Li_2CO_3, Li_2O_2, $LiNO_3$, LiOH or mixtures of two or more thereof. Preference is given to Li_2CO_3. The spray-drying may be followed by post-drying at temperatures of from 100°C to 300°C.

In order to simplify the sintering, a sintering aid can be added in steps 1.1 to 2 in a concentration of from 0.1 to 3% by weight, based on the solids content. The sintering aid is preferably added during preparation of the mixture, step 1.1. The sintering aid employed is preferably a boron oxide, particularly preferably H_3BO_3.

Thin-film electrodes which contain the lithium manganese oxide compounds prepared by the process according to the invention can be produced as follows:

A mixture of the pigment according to the invention, conductive black having a surface area of greater than 50 m^2/g, graphite and a fluorine-containing binder, as well as volatile solvents, such as, for example, N-methylpyrrolidone (NMP) and/or acetone, is prepared. The following amounts are generally employed: pigment: 80 parts by weight, conductive black and graphite: 5 - 15 parts by weight, binder: 5 - 15 parts by weight. The amount of solvent is selected in such a way that the mixture can be sprayed, cast or knife-coated.

The mixture is applied to an electrically conductive collector in one or more operations, and the solvent is evaporated. The applied layer can be sealed by known methods, such as rolling or pressing.

In order to produce a secondary lithium ion battery, a thin-film electrode produced by the process described above is used as cathode, while the anode employed is a lithium metal electrode or a thin-film electrode consisting of graphite, carbon or another material which is capable of taking up lithium electrons, and a suitable binder. These electrodes are assembled together with a separator and an electrolyte and optionally further constituents in a casing to give a secondary battery and charged. Secondary lithium ion batteries produced in this way have excellent service properties.

The lithium manganese oxide intercalation compounds prepared by the process according to the invention have the morphology described in claim 1. They can advantageously be used for the production of particularly thin thin-film electrodes. Secondary lithium ion batteries which contain the lithium manganese oxide spinels according to the invention as active material of the positive electrode are particularly suitable as high-performance batteries.

The invention is described below in greater detail with reference to figures 1 to 3 and an example, but is not restricted thereto.

Fig. 1 shows the size range of the internal pores and the internal pore volume for an Li/Mn spinel in accordance with the example according to the invention

Fig. 2 shows the size range of the internal pores and the internal pore volume of a commercially available Li/Mn spinel having a specific surface area of 1.2 m^2/g

Fig. 3 shows the X-ray diffraction pattern of the spinel precursor compound in accordance with the present invention

Example according to the invention: Preparation of an Li/Mn spinel

1.1 Mixing

712 kg of manganese oxide (Mn_3O_4 from Fermac, Ludwigshafen, after grinding in an Alpine 250 Z pin mill) and 184.5 kg of lithium carbonate (product ground to less than 40 μm from Chemetall, Frankfurt) are mixed for 30 minutes in a drum mixer with 3 knife heads (capacity 2 m^3, Lödige). The following measurement values were obtained from the mixture: bulk density: 0.7 g/ml, tamped density: 1.3 g/ml, specific surface area: 12 m^2/g.

1.2. and 1.3. Heating under N_2 and grinding

The mixture from 1.1 was heated in a gas-heated rotary tube furnace (Elino, length of heating zone 3.2 m, diameter 300 mm). The firing temperature was 750 ± 10°C. 11 m^3 of nitrogen per hour were passed in cocurrent through the tube. The furnace atmosphere was protected against the ambient air by a double flap airlock valve at the tube end, so that the oxygen content in the rotary tube dropped below 1%. The mixture was metered into the tube at about 30 - 40 kg/h. The tube rotated at 2 revolutions per minute. The inclination of the tube was 0.5 degree, so that the residence time of the product in the heating

zone was about 1 hour. A preliminary fraction of a few kilograms of product was discarded. 500 kg of fired product were subsequently collected. The product was ground in a pin mill (Alpine 250 Z). The following measurement values were obtained: bulk density: 0.8 g/ml, tamped density: 1.0 g/ml, specific surface area: 3 m^2/g. About 6 hours after commencement of the synthesis, a sample was taken from the tube outlet and analyzed by X-rays. Numerous sharp diffraction reflections were found (see Figure 3), which indicate the presence of the following crystalline phases: $LiMnO_2$ (35-0749), MnO (7-0230) and Mn_3O_4 (24-0734). No spinel phase was observed. The numbers shown in brackets indicate the assignment of the diffraction reflections to the compounds in the JCPDS file. The carbon content of the sample was 0.39 percent by weight, which indicated substantially complete decomposition of the Li_2CO_3 employed, i.e. to less than 0.4%.

1.4 and 1.5. Heating under N_2 and grinding

The ground fired product from 1.3 was reheated in the gas-heated rotary tube furnace (see above). The firing temperature was 825°C. 10 ± 1 m^3/h of nitrogen were passed in cocurrent through the tube. The furnace atmosphere was protected against the ambient air by a double flap airlock valve at the tube end, so that the oxygen content in the rotary tube was less than 1%. The mixture was metered into the tube at about 25 kg/h. The tube rotated at 2 revolutions per minute. The inclination of the tube was 0.5 degree, so that the residence time of the product in the heating zone was about 1 hour. A preliminary fraction of a few kilograms of product was discarded. 169.5 kg of fired product were subsequently collected. The product was ground in a pin mill (Alpine 250 Z). The following measurement

values were obtained: bulk density: 0.8 g/ml, tamped density: 1.4 g/ml, specific surface area: 1.1 m^2/g.

1.5.1. Repetition of the grinding

Since the product from 1.5 still contained slightly scratching components, the grinding of a part quantity of 54 kg was repeated in a mill with classifier wheel (Alpine ZPS 50). The mill rotor speed was 15,000 rpm, and the classifier wheel rotated at 4000 rpm. The following measurement values of the classifier-ground product were obtained: bulk density: 1.0 g/ml, tamped density: 1.3 g/ml, specific surface area: 1.4 m^2/g. The particle size distribution was as follows: d_{10} = 1.0 μm, d_{50} = 3.0 μm, d_{90} = 14 μm.

2. Heating under an oxidizing atmosphere

An amount of 40 kg of the ground fired product from 1.5.1 was heated in an electrically heated rotary tube furnace. The powder was metered into the tube at about 5.4 kg/h. The firing temperature was 775°C (length of the heating zone 140 cm). 0.6 m^3 per hour of oxygen was passed in cocurrent through the tube (diameter 25 cm). The tube rotated at 4/3 rotations per minute and was paused for 1 minute every quarter rotation so that the residence time of the product in the heating zone reached about 3.3 hours. The inclination of the tube was 0.25 degree. 28.9 kg of lithium manganese oxide spinel were prepared. The following measurement values were obtained: bulk density: 1.0 g/ml, tamped density: 1.1 g/ml, specific surface area: 0.7 m^2/g, pH: 8.5, particle size distribution: d_{10} = 2.7 μm, d_{50} = 7 μm, d_{90} = 23 μm. The X-ray diffraction analysis showed the diffractogram of a phase-pure Li/Mn spinel (analogous to JCPDS 35-0782) and gave a crystallite size of 0.5 μm, evident from sharp diffraction reflections, some of

which were split even at 36 degrees. The power charge was determined, and a value of 108 Ah/kg was found in the 5th discharge (lithium intercalation).

3. Suspension and spray-drying with Li_2CO_3

A suspension of 10 kg of the fired product from 2., 10 liters of water and 100 g of lithium carbonate was stirred in a tank using a Kotthof dispersion unit and dried in a spray drier (Niro Minor) using an atomization wheel. The heating-gas temperature was 350 ± 5°C, and the outlet gas temperature was 130 ± 5°C. The atomizer gas pressure was 4.6 bar. 8.9 kg of Li/Mn spinel having an Li_2CO_3 layer were obtained. The particle size distribution was as follows: d_{10} = 2.3 μm, d_{50} = 5 μm, d_{90} = 15 μm, specific surface area: 0.9 m^2/g. Finally, the powder was dried at 110°C for 1 hour in a vacuum drying cabinet (water-jet vacuum).

In addition, the pore size distribution was determined using the mercury porosymmetry method. Interpores (i.e. pores between particles which were not connected to one another) having a size of 1 - 4 μm were evident. The incremental intrusion volume reached a local maximum of 0.045 ml/g at a pore size of 3 μm. No pores were observed in the range from 0.02 to 1 μm. The powder charge data were determined, and a value of 106 Ah/kg was found in the 5th discharge.

Analytical measurements:

1. Pore size distribution:

The pore size distribution in the pore size range between 0.01 and 100 μm was determined using the mercury porosymmetry method with an Autopore II instrument (in accordance with DIN 66133). Using this

method, internal pores, i.e. the pores within coherent particles and the pores arising from the surface roughness, and interpores, i.e. the pores between different particles which are not connected to one another, can be measured. Pores larger than 50 μm arising from the loose bed of a powder are also measured.

2. Specific surface area:

The specific surface area (BET) was determined using a Ströhlein Areameter from Ströhlein, Düsseldorf, by the one-point difference method of Haul and Dümbgen in accordance with DIN 66131. The pigments were dried at 140°C for at least 12 hours.

3. X-ray diffractograms:

X-ray diffractograms were obtained using the AXS D5000 diffractometer. The crystallite size was calculated from the integral half-value width of the 311 peak using the Debye Scherrer formula and taking into account the usual correction for the apparatus spread.

4. Particle size distribution:

The particle size distribution was determined by laser diffraction in a SYMPATEC HELOS instrument. In this measurement, a spatula tip of the powder to be analyzed was added to the circulating water bath (optical concentration: about 15 - 50%). The particles were distributed by ultrasound for 50 seconds before and during the measurement, which took 10 seconds. This measurement essentially determined the diameter of the coherent agglomerates.

5. Powder charge data:

The powder charge data were determined as follows:

Firstly, auxiliaries were mixed in a mill: 1 g of carbon black (for example Vulcan XC-72 or Ensaco 250) plus 1 g of graphite (SFG 10) plus 2.2 g of PVDF (Aldrich). A coating comprising 2 g of spinel and 0.4 g of auxiliaries in NMP (N-methylpyrrolidone) was stirred using a high-speed stirrer. In order to produce the layer to be tested, the coating was sprayed onto the titanium collector, which had in each case been predried and slightly warmed, in up to four repetitions. The area of the current collector was 1.3 cm^2. Between each application, the coating was homogenized using the high-speed stirrer and immediately processed further in order to counter possible separation of the solids. The coating was sprayed onto the prewarmed titanium collector with the aid of a spray gun (air brush spray gun) and dried. The most critical step for the reproducibility and correctness of the measurement was the weighing of the dried layer on the Ti collector. The layer weighed about 25 mg; it was weighed to a resolution of 0.1 mg, corresponding to an error of 0.4%, in the case of differential weighing a maximum of 0.8%, but on average less.

The electrodes were dried for at least 12 hours at 120°C in an oil-pump vacuum before they were assembled into an electrochemical cell in a glove box filled with argon. The anode used was lithium metal (Aldrich, 99.9%, 0.75 mm thickness), and the commercially available electrolyte solution LP 30 (1M $LiPF_6$ in ethylene carbonate/dimethyl carbonate 1:1, Merck) was furthermore used. The separator was a glass nonwoven with a thickness of about 2 mm. The geometry of the charge measurement cells is described in P. Novák,

W. Scheifele, F. Joho, O. Haas, *J. Electrochem. Soc.* **142**, 2544 (1995), see there in particular figure 1 (although the reference electrode shown there was not used).

The charging and discharging were carried out in the potential range between 3.3 and 4.4 volts with constant currents of 10 μA per milligram of oxide, which resulted in charging and discharging times in the order of greater than 10 hours in each case.

6. Method for determination of the pore volume

The pore volume was determined as follows: the pore size distribution in the pore size range between 0.01 and 100 μm was determined using the mercury porosymmetry method with an Autopore II instrument (in accordance with DIN 66133).

Patent Claims:

1. A lithium intercalation compound containing lithium manganese oxide and having a spinel structure for thin-film electrodes, where the lithium intercalation compound has

   - a specific surface area, determined by the BET method, of from 0.3 to 5 m^2/g,

   - a particle size, determined from the d_{50} value, of greater than 0.5 μm,

   - a diameter, determined from the d_{90} value, of 30 μm or less, and an internal pore volume of less than 0.05 ml/g and has a pronounced crystal structure.

2. A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claim 1, where the internal pore volume is less than 0.03 ml/g.

3. A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claims 1 and 2, where the specific BET surface area is from 0.5 to 1.9 m^2/g.

4. A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claims 1 and 2, where the specific BET surface area is from 0.6 to 1.5 m^2/g.

5. A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claims 1 to 4, where the

particle size, determined from the d_{50} value, is greater than 1 μm.

6. A lithium intercalation compound having a spinel structure and containing lithium manganese oxide as claimed in claims 1 to 5, where the diameter, determined from the d_{90} value, is less than 25 μm.

7. A lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claims 1 to 5, where the diameter, determined from the d_{90} value, is less than 20 μm.

8. A process for the preparation of a lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claim 1, by

a) preparation of an intimate mixture of one or more lithium compounds and one or more manganese compounds, where at least one of these compounds or the sum of all compounds contains sufficient active oxygen that the number of equivalents of active oxygen is equal to or greater than the number of lithium atoms, and heating at from 600°C to 1000°C in a non-oxidizing atmosphere, followed by grinding, giving a particulate, crystalline spinel precursor compound;

b) heating the crystalline spinel precursor compound in an oxidizing atmosphere at from 500°C to 800°C with a residence time of from 0.5 to 10 hours.

9. A process for the preparation of a lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claim 1, by

a) a1) preparation of an intimate mixture of Li_2O_3 and Mn_3O_4,

a2) heating at from 600°C to 1000°C under nitrogen, argon or another non-oxidizing atmosphere with a residence time of from 15 to 120 minutes in a rotary tube furnace,

a3) grinding the heated mixture to give a particulate, crystalline precursor compound;

b) heating of the spinel precursor compound in an oxidizing atmosphere at from 500°C to 800°C with a residence time of from 0.5 to 10 hours.

10. A process for the preparation of a lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claim 9, where the heating in a2) and grinding in a3) are carried out two or more times.

11. A process for the preparation of a lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claims 8 to 10, where the particulate, crystalline spinel precursor compound consists of the three phases MnO, $LiMnO_2$ and Mn_3O_4.

12. A process for the preparation of a lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claim 9, where the heating in an oxidizing atmosphere is carried out in a rotary tube furnace at a temperature of from 700°C to 800°C with a residence time of from 0.5 to 6 hours.

13. A process for the preparation of a lithium intercalation compound containing lithium manganese oxide and having a spinel structure as claimed in claim 9, where the heating in an oxidizing atmosphere is carried out in a stationary furnace at a temperature of from 650°C to 750°C with a residence time of greater than 5 hours.

14. A process as claimed in one of claims 8 to 13, where, after the heating in an oxidizing atmosphere, the resultant solid is suspended in water with addition of one or more alkaline lithium compounds, and the suspension is spray-dried at a temperature of from 100°C to 400°C.

15. A process as claimed in claim 14, where the alkaline lithium compound is Li_2CO_3, Li_2O_2, $LiNO_3$, LiOH or a mixture of two or more of these compounds.

16. A process as claimed in one of claims 8 to 15, where the intimate mixing is carried out in the presence of a sintering aid in a concentration of from 0.1 to 3%, based on the weight of the solids employed.

17. A process as claimed in claim 16, where the sintering aid is a boron oxide.

18. A process as claimed in claim 17, where the boron oxide is H_3BO_3.

19. A thin-film electrode for secondary lithium ion batteries containing lithium manganese oxide as claimed in claim 1 as the active material.

20. A secondary lithium ion battery containing lithium manganese oxide as claimed in claim 1 as the active material of the positive electrode.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) **Weltorganisation für geistiges Eigentum**
Internationales Büro

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(74) **Anwalt: HONEIT, Ute**; Emtec Magnetics GmbH, Patente und Lizenzen, Kistlerhofstrasse 70, D-81379 München (DE).

(81) **Bestimmungsstaaten** *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) **Bestimmungsstaaten** *(regional)*: ARIPO-Patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI-Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Veröffentlicht:
— *Mit internationalem Recherchenbericht.*
— *Vor Ablauf der fur Anderungen der Anspruche geltenden Frist; Veröffentlichung wird wiederholt, falls Anderungen eintreffen.*

Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkurzungen wird auf die Erklarungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regularen Ausgabe der PCT-Gazette verwiesen.

(54) **Title:** LITHIUM INTERCALATION COMPOUNDS CONTAINING LITHIUM MANGANESE OXIDE

(54) **Bezeichnung:** LITHIUMMANGANOXID ENTHALTENDE LITHIUMINTERKALATIONSVERBINDUNGEN

(57) **Abstract:** The invention relates to improved lithium intercalation compounds containing lithium manganese oxide, having a spinell structure and a special morphology for thin-film electrodes. The invention further relates to a method for the production of said compounds, electrodes produced from said compounds and secondary lithium batteries with lithium intercalation compounds containing lithium manganese oxide as an active material for the positive electrode, offering high energy and able to be produced in an inexpensive manner in addition to being ecologically friendly and safe.

(57) **Zusammenfassung:** Die Erfindung betrifft verbesserte, Lithiummanganoxid enthaltende Lithiuminterkalationsverbindungen mit Spinellstruktur und beson derer Morphologie für Dünnfilmelektroden, ein Verfahren zu deren Herstellung, daraus hergestellte Elektroden sowie sekundäre Lithiumionenbatterien mit Lithiummanganoxid enthaltenden Lithiuminterkalationsverbindungen als aktives Material der positiven Elektrode, die eine hohe Leistung aufweisen und preisgünstig herstellbar, umweltfreundlich und sicher sind.

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10/031933

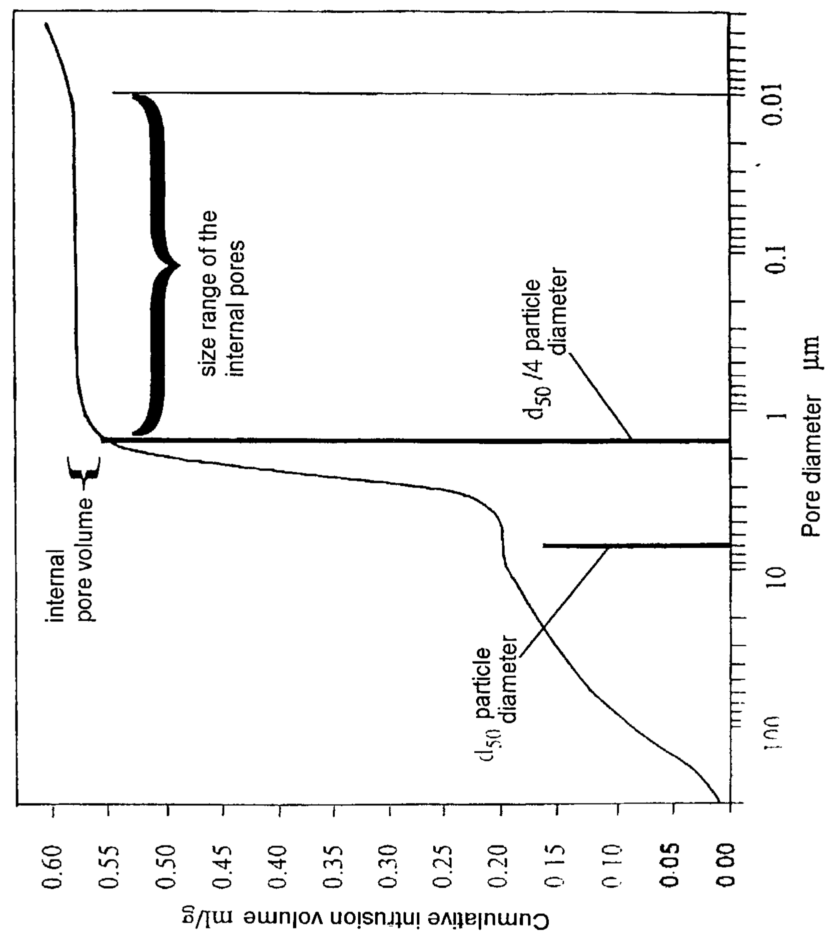
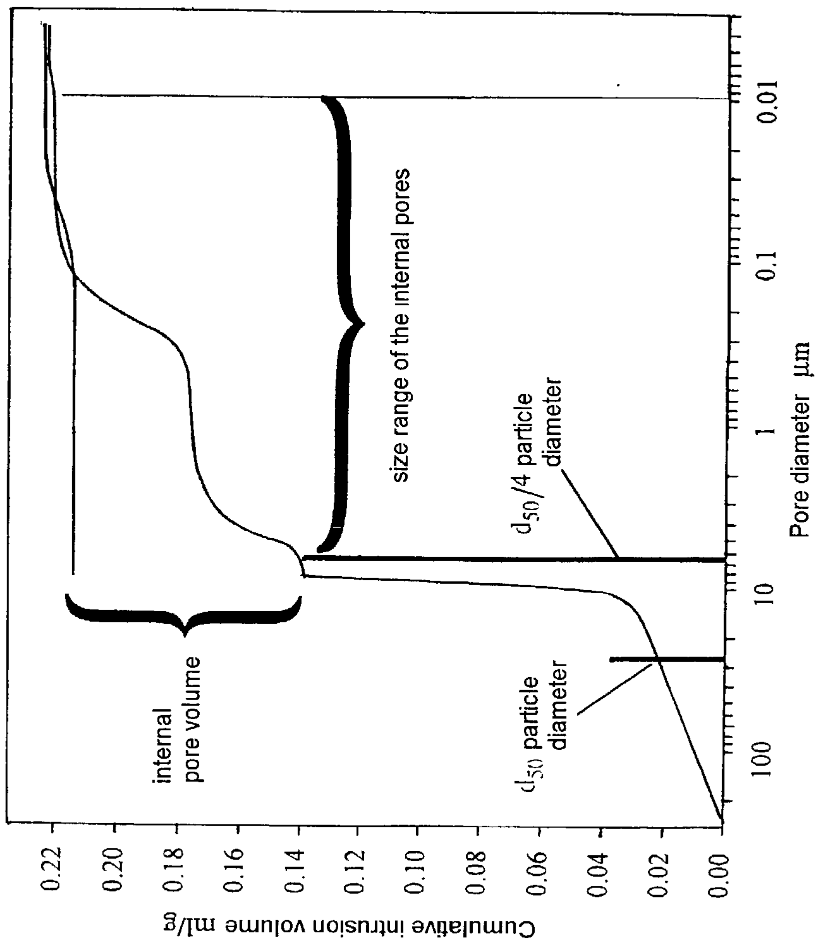


Fig 1


Cumulative intrusion volume ml/g
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Pore diameter µm
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10
1
0.1
0.01
internal pore volume
size range of the internal pores
$d_{50}/4$ particle diameter
d_{50} particle diameter

Fig. 2

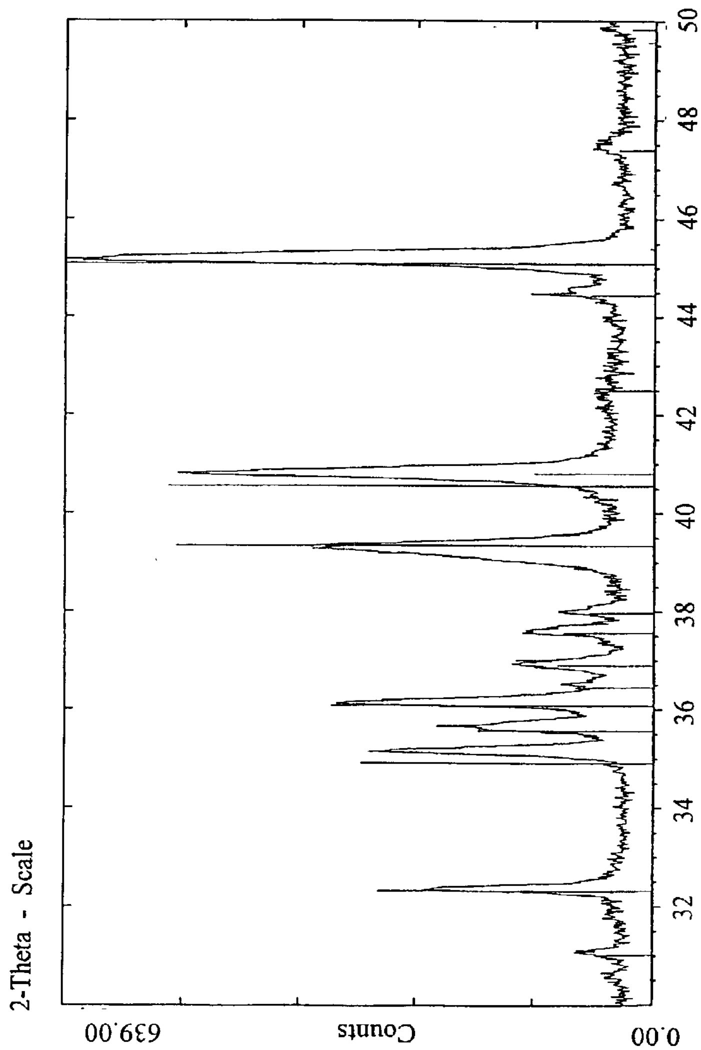

Fig. 3

Declaration and Power of Attorney For Utility or Design Patent Application

Erklärung für Patentanmeldungen zur Gebrauchseignung und Entwicklung
mit Vollmacht

German Language Declaration

Als nachstehend benannter Erfinder erkläre ich hiermit an Eides Statt:

As a below named inventor, I hereby declare that:

daß mein Wohnsitz, meine Postanschrift und meine Staatsangehörigkeit den im nachstehenden nach meinem Namen aufgeführten Angaben entsprechen, daß ich nach bestem Wissen der ursprüngliche, erste und alleinige Erfinder (falls nachstehend nur ein Name angegeben ist) oder ein ursprünglicher, erster und Miterfinder (falls nachstehend mehrere Namen aufgeführt sind) des Gegenstandes bin, für den dieser Antrag gestellt wird und für den ein Patent für die Erfindung mit folgendem Titel beantragt wird:
LITHIUMMANGANOXID ENTHALTENDE LITHIUMINTERKALATIONSVERBINDUNGEN

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled
LITHIUM INTERCALATION COMPOUNDS CONTAINING LITHIUM MANGANESE OXIDE

deren Beschreibung hier beigefügt ist, es sei denn (in diesem Falle Zutreffendes bitte ankreuzen), diese Erfindung

the specification of which is attached hereto unless the following box is checked:

☒ wurde angemeldet am 15 juli 2000
unter der US-Anmeldenummer 10/031,933
und wurde am ____________ abgeändert (falls zutreffend)
oder

unter der PCT internationalen Anmeldungsnummer PCT/EP00/06766 und wurde am __________ abgeändert (falls zutreffend).

☒ was filed on July 15, 2000 as
United States Application Number 10/031,933
and was amended on ________________ (if applicable)
or,

PCT International Application Number PCT/EP00/06766 and was amended on ________________ (if applicable).

Ich bestätige hiermit, daß ich den Inhalt der oben angegebene Patentanmeldung, einschließlich der Ansprüche, die eventuell durch einen oben erwähnten Zusatzantrag abgeändert wurde, durchgesehen und verstanden habe.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

Ich erkenne meine Pflicht zur Offenbarung jeglicher Informationen an, die zur Prüfung der Patentfähigkeit in Einklang mit Titel 37, Code of Federal Regulations, § 1.56 von Belang sind.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

Ich beanspruche hiermit ausländische Prioritätsvorteile gemäß Title 35, US-Code, § 119 (a)-(d), bzw. § 365(b) aller unten aufgeführten Auslandsanmeldungen für Patente oder Erfinderurkunden, oder § 365(a) aller PCT internationalen Anmeldungen, welche wenigstens ein Land ausser den Vereingten Staaten von Amerika benennen, und habe nachstehend durch ankreuzen sämtliche Auslandsanmeldungen für Patente bzw. Erfinderurkunden oder PCT internationale Anmeldungen angegeben, deren Anmeldetag dem der Anmeldung, für welche Priorität beansprucht wird, vorangeht.

I hereby claim foreign priority under Title 35, United States Code §119 (a-d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designated at least one country other than the United States, listed below. I have also identified below, by checking the "No" box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed:

Prior Foreign Applications
Frühere ausländische Anmeldungen

			Priority Claimed Prioritätsanspruch	
199 35 091.4	GERMANY	27 JULY 1999	☒	☐
(Number) (Nummer)	(Country) (Land)	(Day/Month/Year Filed) (Tag/Monat/Jahr der Anmeldung)	Yes Ja	No Nein
			☐	☐
(Number) (Nummer)	(Country) (Land)	(Day/Month/Year Filed) (Tag/Monat/Jahr der Anmeldung)	Yes Ja	No Nein

☐ Zusätzliche einstweilige Anmeldungsnummern sind im Prioritätsanhang aufgeführt.

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto.

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Ich beanspruche hiermit Prioritätsvorteile unter Title 35, US-Code, § 119(e) aller US-Hilfsanmeldungen wie unten aufgezählt.

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

(Application Number)
(Aktenzeichen)

(Day/Month/Year Filed)
(Tag/Monat/Jahr der Anmeldung)

(Application Number)
(Aktenzeichen)

(Day/Month/Year Filed)
(Tag/Monat/Jahr der Anmeldung)

(Application Number)
(Aktenzeichen)

(Day/Month/Year Filed)
(Tag/Monat/Jahr der Anmeldung)

☐ Zusätzliche einstweilige Anmeldungsnummern sind im ergänzenden Prioritätsanhang aufgeführt.

☐ Additional provisional application numbers are listed on a supplemental priority sheet attached hereto.

Ich beanspruche hiermit die mir unter Title 35, US-Code, § 120 zustehenden Vorteile aller unten aufgeführten US-Patentanmeldungen bzw. § 365(c) aller PCT internationalen Anmeldungen, welche die Vereinigten Staaten von Amerika benennen, und erkenne, insofern der Gegenstand eines jeden früheren Anspruchs dieser Patentanmeldung nicht in einer US-Patentanmeldung, bzw. PCT internationalen Anmeldung in in einer gemäß dem ersten Absatz von Title 35, US-Code, § 112 vorgeschriebenen Art und Weise offenbart wurde, meine Pflicht zur Offenbarung jeglicher Informationen an, die zur Prüfung der Patentfähigkeit in Einklang mit Title 37, Code of Federal Regulations, § 1.56 von Belang sind und die im Zeitraum zwischen dem Anmeldetag der früheren Patentanmeldung und dem nationalen oder im Rahmen des Vertrags über die Zusammenarbeit auf dem Gebiet des Patentwesen (PCT) gültigen internationalen Anmeldetags bekannt geworden sind.

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365(c) of any PCT international application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

(Application No.) (Aktenzeichen)	(Day/Month/Year Filed) (Tag/Monat/Jahr eingereicht)	(Status) (patentiert, schwebend, aufgegeben) (patented, pending, abandoned)
(Application No.) (Aktenzeichen)	(Day/Month/Year Filed) (Tag/Monat/Jahr eingereicht)	(Status) (patentiert, schwebend, aufgegeben) (patented, pending, abandoned)

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☐ Additional U.S. or international application numbers are listed on a supplemental priority sheet attached hereto.

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German Language Utility or Design Patent Application Declaration

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